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Influence of reacting gas content on structural and electro-physical properties of nanostructured diamond films grown by chemical vapor deposition with crossed E/H field glow discharge stabilization

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ABSTRACT

The method and setup for polycrystalline diamond films deposition from the gas-phase using the direct current (DC) glow discharge stabilized by crossed E/H field are presented. The mentioned method was used for the preparation of nanostructured diamond films. The nanostructure formation was realized by N_2 addition to $Ar/CH_4/H_2$ plasma. The detailed study of electro-physical, morphological and structural properties was done using simple two-electrodes scheme of resistivity measurements, atomic force and scanning electron microscopies as well as Raman spectroscopy. The data of electro-physical measurements is in good correlation with the data of optical measurements and complement each other showing the complete picture of the processes of modification of the diamond films structure induced by nitrogen atoms incorporation.

1. Introduction

The development of the processes for preparation of the nanostructured diamond films is an important step in the way for creation of new carbon-based materials. It was ascertained that reduction of the crystalline sizes in polycrystalline diamond films causes the substantial decrease in the growth of surface roughness as well as induces the changes of electrical, optical and recombination properties inherent to these films [1–5]. They become attractive for electrochemical application, tribology, electronic and optical devices, supercapacitors, sensors or fuel cells as well as medicine [6].

The most developed methods for preparation of the nanostructured diamond films are the following.

Firstly, nanostructured diamond films can be produced by cathodic arc or magnetron sputtering in the presence of a relatively high gas pressure to favor the aggregation of sp^2 clusters to be incorporated in the films.

Secondly, supersonic cluster beam deposition can also be used to grow nanostructured thin films where the original carbon cluster structure is substantially maintained after the deposition [7]. These films are characterized by a memory effect, i.e. they are partially reminiscent of the precursor clusters. Small carbon clusters mainly have chain or ring structures, where the larger clusters have the tendency to form three-dimensional cage-like structures characterized by sp^2 coordination. Peculiar to these films is often the presence of carbon sp^1 chains.

Thirdly, X.T. Zhou developed a new process to get a stable substrate current and high-density diamond nucleation on mirror-polished silicon by using double bias-assisted (hot filament chemical vapor deposition) HFCVD method [8]. The preparation process included substrate pre-treatment, Ta filament carbonization, nucleation and growth of diamond film.

Fourthly, nanocrystalline diamond coatings can be prepared by microwave plasma chemical vapor deposition (MWCVD). The first approach involves an increase of the methane concentration in the conventional CH_4/H_2 gas mixture, leading to enhanced secondary nucleation rate, the second one – partial or complete substitution of hydrogen by argon or nitrogen, resulting in change of the growth mechanism by inclusion of new film-forming species [9]. Also, the nanostructured diamond films can be produced by plasma enhanced chemical vapor deposition (PECVD) through N_2 addition to $Ar/CH_4/H_2$ plasma [10–15]. Such films have become very attractive materials for microelectronics applications, since such films with N_2 doping have been shown to have moderate *n*- and *p*-type semiconductor characteristics. Both theoretical calculations and experimental data show that the preferential incorporation of N atoms into grain boundaries of N-doped

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nanocrystalline carbon films would cause large clustering and disordering of graphite-like sp^2-bonded carbon. Recently, nanowires consisting of diamond core and sheathed with sp^2-bonded carbon about 1 nm in thickness are observed in N-doped nanocrystalline carbon films with addition up to 10% of N_2 [16].

Nowadays, microwave discharge is most often used for the working gas activation, but the equipment necessary for the process is expensive enough and complicated. The synthesis method can be substantially simplified if the magnetic field glow discharge is used to excite the gas mixture.

Therefore, in the present work the deposition method and corresponding setup for diamond films (coatings) deposition based on the direct current glow discharge stabilized by crossed E/H fields (CVD) were developed. The aim of the work is the detailed study of the changes in the structural and electrical properties of nanostructured diamond films induced by various concentrations N_2 addition to $Ar/CH_4/H_2$ plasma during the growth using the developed method.

2. Experimental details

2.1. Nanostructured diamond films growth

In the present work the method and setup for polycrystalline diamond film deposition where activation of the gas phase is realized through the DC glow discharge in crossed E/H fields are developed and successfully used (Fig. 1). The presence of crossed magnetic field in this scheme of gas discharge leads to stabilization of the normal glow discharge in a wide range of discharge currents at the current density higher than 1 A/cm^2. Herewith, the power density used for activation of the operation gas reaches 1000 W/cm^3, which corresponds to energetic characteristics typical for the high-efficient industrial equipment for synthesis of diamond coatings. Contrary to the classic scheme of glow discharge used for activation of the gas phase (where substrate holder is one of the electrodes (anode) for discharge) in the construction of developed equipment the substrate holder is electrically isolated from the anode as well as from cathode. Nevertheless, at the discharge excitation the substrate acquires the negative (floating) potential relatively to grounded anode and reaction chamber walls. The value of the potential can reach 40% from the voltage between anode and cathode and depends on discharge conditions. It results in additional bombardment of the substrate surface by plasma ions. To provide formation of nanostructured diamond coatings in the glow discharge, N_2 were added to $Ar/CH_4/H_2$ operation mixture. Fig. 2 shows the discharge for synthesis of diamond coating from the $Ar/CH_4/H_2$ mixture. This figure gives the full presentation about the type of discharge in the chamber. In the presence of magnetic field, the diffuse glow discharge transforms in current channel mode; the current channel rotates with the frequency close to 150…200 Hz. It allows achieving the high density of plasma in the current channel (up to 1000 W/cm^3). In the photo with 1/800 s exposition time, one can see that the discharge is localized as a narrow cord. At the exposition time 1/200 s, namely within 5 ms, the current channel during its rotation makes a complete circle, and in the photo one can see the surface which depicts the current channel.

2.2. Resistivity measurements

The resistivity measurements of coatings and films can be performed in various ways. The choice of the technique depends on specific conditions related to coating characteristics as well as diamond films substrate characteristics. In our case, conducting doped Si plates serve as substrates, which allow applying the simple two-electrodes scheme for measurements. It is noteworthy that, providing the mentioned measuring scheme, it is very important to implement full contact of measuring electrode over the whole area of its touching to the surface of the film. When providing the latter, the probe electrode that contacts with the coating surface was moistened with gel electrolyte based on liquid soap. To avoid the polarization effect at the current conduction through liquid electrolyte film on the results of resistivity measurements, the scheme with alternating current power supply was used. Fig. 3 (insertion) shows the scheme of electrical resistance measurements of studied samples $R_x = R_a + R_{si} + R_e$, where R_a, R_{si} and R_e are electrical resistances of the diamond film, substrate and electrode, respectively. The measuring current was tuned by the resistance R_0 within the range3 to 5 mA. As an alternating power supply, the generator G3-53 was used. It is characterized by the utmost oscillation frequency of 20 kHz. The sample resistance was obtained from the equation:

$$Rx = (Ux \cdot Ro)/(Ugen–Ux). \quad (1)$$

The measurement of Si substrate electrical resistance (R_{Si}) before deposition of coatings at different frequencies indicates that the polarization effect when the current passes through the electrolyte film has a

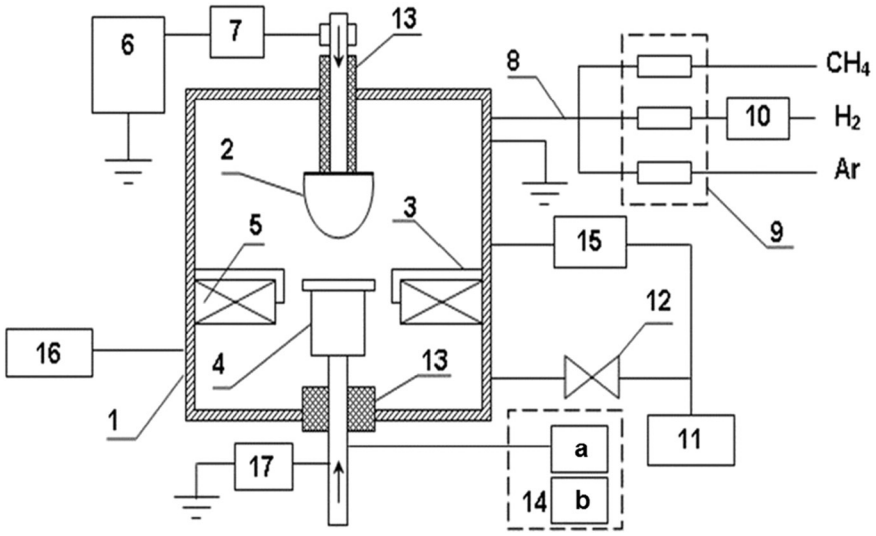

Fig. 1. The scheme of the setup for diamond coatings synthesis: 1 – vacuum chamber; 2 – water-cooled molybdenum cathode; 3 – circle-type anode;4 – water-cooled substrate holder; 5 – permanent ring magnet; 6 – high voltage power supply; 7 – devices for control of discharge current and voltage; 8 – gas-precursor supply; 9 – gas flux regulator; 10 – water supply generator; 11 – vacuum pump; 12 – vacuum valve; 13 – insulators; 14 – temperature control system (a - thermocouples, b – pyrometer); 15 – pressure control system; 16 – detector IPDO-2 with registration block; 17 – device for substrate potential control.